

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-289168

(43)Date of publication of application : 17.10.2000

(51)Int.Cl. B32B 27/36

(21)Application number : 11-097364 (71)Applicant : MITSUBISHI POLYESTER FILM
COPP

(22)Date of filing : 05.04.1999 (72)Inventor : KUNUGIHARA KAZUHIRO
MIKI TAKATOSHI

(54) POLYESTER FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a film sealing an oligomer precipitated on a surface of the film from a polymer by heat treating or the like.

SOLUTION: In the polyester film comprising a coating layer provided on at least one surface of the film, an oligomer amount of a surface of the layer after heat treating at 150°C for 10 min is 0.60 mg/m² or below, and the layer contains 10 to 100 wt.%; of a polyvinyl alcohol, and a cured silicone resin coating film layer is provided on the coating layer of the film.

LEGAL STATUS

[Date of request for examination] 05.01.2006

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the polyester film and the mold releasing film which can close a deposit of oligomer by the spreading layer under an elevated temperature by preparing in more detail the spreading layer which consists of a specific presentation about the polyester film and the mold releasing film which prepared the spreading layer which closes a deposit of oligomer.

[0002]

[Description of the Prior Art] Since it has the outstanding properties, such as a mechanical strength, dimensional stability, surface smoothness, thermal resistance, chemical resistance, and an optical property, and excels in cost performance, the polyester film represented by polyethylene terephthalate or polyethylenenaphthalate is used in various kinds of applications. However, if processing of a film and a service condition are also diversified, for example, polyester film is left at an elevated temperature 100 degrees C or more as an application is diversified, since the oligomer which has encroached on the film front face from the interior deposits, various problems have arisen by processing or using a film on such conditions. Moreover, although various kinds of spreading films are proposed for the purpose of the surface treatment of polyester film, the problem which promotes a deposit of oligomer depending on the presentation to apply has arisen.

[0003] Although reduction of the oligomer contained by solid state polymerization in a raw material is conventionally aimed at as an approach of preventing a deposit of oligomer and raising the hydrolysis-proof nature of polyester film using an end blockade agent etc. has been performed, it has not resulted till the place with which are satisfied of deposit prevention of oligomer. As an example using polyester film, in order to protect the adhesive face of a binder etc., there is a mold releasing film which coated silicone resin. The conventional mold releasing film has prepared the easy-bonding layer, in order to improve the adhesive property of silicone resin and polyester film. However, when temperature is given to a film by heat treatment in a production process etc., in the easy-bonding layer, the effectiveness which closes a deposit of oligomer is not seen, but a deposit of oligomer is promoted in the paint which blended polyester, the processing conditions in a production process are restricted, or it poses [the oligomer which has deposited invades into a binder, serves as a foreign matter, and] a problem from the silicon coat layer.

[0004]

[Problem(s) to be Solved by the Invention] This invention makes it a solution technical problem to close the oligomer which deposits on a film front face from a polymer by heat treatment etc.

[0005]

[Means for Solving the Problem] As a result of repeating examination wholeheartedly in view of the above-mentioned actual condition, by forming the spreading layer which consists of a certain specific presentation, this invention persons do the knowledge of polyester film with very few oligomer deposits being obtained, and came to complete this invention. That is, for the summary of this invention, it sets on the film which comes to prepare a spreading layer in one [at least] front face of polyester film, and

the amount of oligomer of the spreading layer front face after heat treatment is 0.60 mg/m² for 10 minutes at 150 degrees C. It consists in the polyester film which is the following and is characterized by a spreading layer containing polyvinyl alcohol ten to 100% of the weight, and the mold releasing film characterized by having a hardening silicone resin coat on the spreading layer of the polyester film concerned.

[0006]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. Typically as polyester in this invention, Polly 1, 4-cyclohexane dimethylene terephthalate, etc. more than whose 80 mol % of the polyethylene -2 more than whose 80 mol % of the polyethylene terephthalate more than whose 80 mol % of a configuration unit is ethylene terephthalate, and a configuration unit is ethylene -2 and 6-naphthalate, 6-naphthalate, and a configuration unit is 1 and 4-cyclohexane dimethylene terephthalate are mentioned. Polyethylene isophthalate, Polly 1, 4-butylene terephthalate, etc. are mentioned to others.

[0007] As copolymerization components other than the above-mentioned dominance constituent For example, propylene glycol, 1, 3-butylene glycol, 2, 3-butylene glycol, Neopentyl glycol, a trimethylene glycol, tetramethylene glycol, Hexamethylene glycol, a diethylene glycol, triethylene glycol, Diol components, such as a polyethylene glycol, a polytetramethylene glycol, and a polyalkylene glycol, Isophthalic acid, 2, 7-naphthalene dicarboxylic acid, 5-sodium sulfoisophthalate, Ester plasticity derivatives, such as oxalic acid, a malonic acid, a succinic acid, an adipic acid, an azelaic acid, a sebacic acid, diphenyl ether dicarboxylic acid, and oxy-monocarboxylic acid, can be used. Moreover, as polyester, the blend of a small rate with other resin can also be used besides a homopolymer or a copolymer.

[0008] the limiting viscosity of the polyester film of this invention -- usually -- 0.40 to 0.90 -- desirable - 0.45 to 0.80 -- it is the range of 0.50-0.70 still more preferably. When there is an inclination for the mechanical strength of a film to become [limiting viscosity] weak less than by 0.40 and limiting viscosity exceeds 0.90, melt viscosity becomes high, a load may be applied to an extruder or problems, like a manufacturing cost is applied may arise. Although the formula which reduces the oligomer of a film and which is made to reduce the amount of oligomer in a polymer beforehand by solid state polymerization, and lessens the oligomer of the last film if an approach is carried out is used conventionally, in order that limiting viscosity may become high or a process may increase, in the case of solid state polymerization, there is a problem on which cost goes up. Moreover, when melting temperature is high or the residence time becomes long with the extruder of a film production process, the effectiveness of having reduced oligomer is no longer seen.

[0009] The polyester film of this invention may contain an addition particle, a deposit particle, other catalyst residue, etc. as a film surface projection formation agent in order to give slipping nature. The class of these projection formation agents, magnitude, and loadings are suitably chosen according to slipping nature, transparency, etc. which are made into the object. Moreover, polyester film may contain an antistatic agent, a stabilizer, lubricant, a cross linking agent, an antiblocking agent, the antioxidant, the ultraviolet ray absorbent, the beam-of-light cutoff agent, the coloring agent, etc. if needed.

[0010] Moreover, the polyester film of this invention may be multilayer structure, and some of those layers may be formed by polymers other than polyester in this case. The polyester film of this invention prepares a spreading layer in one [at least] front face, and is the amount of oligomer of the spreading layer front face after heat treatment preferably two or less 0.60 mg/m for 10 minutes at 150 degrees C 0.50 mg/m² They are 0.40 mg/m² still more preferably hereafter. It considers as the following. The amount of surface oligomer is 0.60 mg/m². It becomes [the application of polyester film is limited, or oligomer occurs so much under an elevated temperature, and] a foreign matter and is not desirable when exceeding. Moreover, when it considers as a mold releasing film, a foreign matter mixes and is not desirable in an adhesives layer.

[0011] In order to achieve the above-mentioned object, in this invention, the deposit prevention layer of oligomer is formed in a film front face by spreading, and the layer concerned makes polyvinyl alcohol preferably what is contained 30 to 90% of the weight still more preferably 20 to 90% of the weight ten

to 100% of the weight. In less than 10 % of the weight, the oligomer closure effectiveness does not have [the insufficiency of **] the desirable content of polyvinyl alcohol.

[0012] The polyvinyl alcohol used by this invention can be compounded by the usual polymerization reaction, and it is desirable that it is water solubility. Although especially the polymerization degree of polyvinyl alcohol is not limited, the thing of 300-40000 is usually used preferably 100 or more. When polymerization degree is 100 or less, there is an inclination for the water resisting property of a spreading layer to fall. Although especially the saponification degree of the polyvinyl alcohol used by this invention is not limited, more than 70 mol % and the polyvinyl acetate saponification object which are more than 80 mol % and less than [99.9 mol %] preferably are usually used practically.

[0013] In the oligomer deposit prevention layer in this invention, binder resin water-soluble [other than the above-mentioned polyvinyl alcohol] or water-dispersion may be used together if needed. As this binder resin, polyester, polyurethane, acrylic resin, vinyl resin, an epoxy resin, amide resin, etc. are mentioned, for example. As for these, each skeletal structure may have the composite construction substantially by copolymerization etc. As binder resin with a composite construction, acrylic resin graft polyester, acrylic resin graft polyurethane, vinyl resin graft polyester, vinyl resin graft polyurethane, etc. are mentioned, for example. The loadings of a binder component have the desirable range below 30 weight sections to a pan below 50 weight sections in the weight section to a spreading layer.

Furthermore in the spreading layer of the film of this invention, the crosslinking reaction nature compound may be included if needed.

[0014] It is chosen from a polyfunctional low molecular weight compound and high molecular compounds, such as a vinyl compound of compounds, such as methylol-izing or a urea system formed into the ARUKI roll, a melamine system, a guanamine system, an acrylamide system, and a polyamide system, polyamine, an epoxy compound, an oxazoline compound, an aziridine compound, a block isocyanate compound, a silane coupling agent, a titanium coupling agent, a zirconium-aluminum system coupling agent, a metal chelate, an organic-acid anhydride, organic peroxide, heat, or photoreaction nature, and a photopolymer, as a crosslinking reaction nature compound.

[0015] A crosslinking reaction nature compound can improve coherent [of an easily-adhesive resin layer], surface hardness, abrasion-proof nature, solvent resistance, and a water resisting property by carrying out crosslinking reaction to the functional group which the resin mainly contained in an easily-adhesive resin layer has. When the functional group of easily-adhesive resin is a hydroxyl group, for example, as a crosslinking reaction nature compound A melamine system compound, a block isocyanate compound, an organic-acid anhydride, etc. are desirable. When the functional groups of easily-adhesive polyester are an organic acid and its anhydride, as a crosslinking reaction nature compound Epoxy compound, A melamine system compound, an oxazoline system compound, a metal chelate, etc. are desirable. When the functional groups of easily-adhesive resin are amines, as a crosslinking reaction nature compound, epoxy compound etc. is desirable and it is desirable to choose and use what has the high functional group and the crosslinking reaction effectiveness which are included in easily-adhesive resin.

[0016] As long as two or more organic functions of reactant functional groups are surely contained in 1 molecule, even if a crosslinking reaction nature compound is a low molecular weight compound, it may be any of a macromolecule polymer which have a reactant functional group. The loadings of a crosslinking reaction nature compound have the range desirable in the weight section to an easily-adhesive resin layer below 15 weight sections below 30 weight sections to especially a pan below 50 weight sections. Furthermore in the easily-adhesive resin layer of this invention, the inactive particle may be included if needed for slipping nature amelioration of a spreading layer.

[0017] As an inactive particle, there are an inorganic inactive particle and an organic inactive particle, and a silica sol, alumina sol, a calcium carbonate, titanium oxide, etc. are mentioned as an inorganic inactive particle, for example. As an organic inactive particle, the organic particle by polystyrene system resin, Pori acrylic resin, and polyvinyl system resin represented by independent, or the particle containing a copolymer or the bridge formation particle which compounded these and a bridge formation component is mentioned. As for especially these inactive particles, it is desirable that

softening temperature or about 200 degrees C or more of 250 more degrees C or more of decomposition temperature are 300 degrees C or more. When the mean particle diameter (d) of an inactive particle sets average thickness of an easily-adhesive resin layer to (L), it is desirable to choose so that it may be satisfied with $1/3 \leq d/L \leq 3$ and a pan of the relation of $1/2 \leq d/L \leq 2$.

[0018] The easily-adhesive resin layer of this invention may be carrying out little content of the additives, such as a surfactant, a defoaming agent, a spreading nature amelioration agent, a thickener, a low-molecular antistatic agent, organic system lubricant, an antioxidant, an ultraviolet ray absorbent, a foaming agent, a color, and a pigment, if needed. Although these additives may be used independently, two or more sorts may be used together if needed. The spreading layer of the film of this invention may be formed only in one side of polyester film, and may be formed in both sides. When forming only in one side, the spreading layer of another kind can be made to be able to form in the reverse side if needed, and the property of further others can also be given. In addition, in order to improve the spreading nature to the film of coating liquid, and an adhesive property, a chemical treatment, electrodischarge treatment, etc. may be performed to the film before spreading.

[0019] Especially the thickness of a spreading layer has the desirable range of 0.03-0.2 micrometers further 0.02-0.5 micrometers 0.01-2 micrometers. When the effectiveness of oligomer deposit prevention sufficient when the thickness of a spreading layer is less than 0.01 micrometers may not be acquired and it exceeds 2 micrometers, there is an inclination which becomes inadequate [blocking resistance]. The range of 20-75 micrometers of film thickness of this invention is 10-100 micrometers usually 20-50 micrometers still more preferably. When this range is exceeded, the handling nature of a film may worsen or a manufacturing cost may rise. The film haze value after heat treatment is 1.0 - 6.0% usually 2.0 - 5.0% of range still more preferably 1.5 to 5.0% preferably for 10 minutes at 150 degrees C. If a film haze will need to lessen the content of an addition particle in order that less than 1.0% of film may lower a film haze, and it does so, the slipping nature of a film will get worse, and workability will worsen. When a film haze exceeds 6.0%, there is a possibility that an application may be limited.

[0020] As the manufacture approach of biaxial-stretching polyester film, a well-known approach is employable. For example, mix a required additive with the polyester chip dried beforehand, carry out the hopper charge at an extruder, carry out melting kneading at the temperature of 200-300 degrees C with an extruder, and it extrudes in the shape of a sheet from a die. the sheet which quenched on casting drum (revolution cooling drum) about 70 degrees C or less, obtained the non-extended sheet, and was obtained -- length -- and -- or the approach of extending in a longitudinal direction for the area scale factor of 9 times or more preferably, and performing heat setting in it at the temperature of further 120-200 degrees C 4 or more times is employable.

[0021] Although especially the approach of forming a spreading layer in the front face of biaxial-stretching polyester film is not restricted, it is in process and the approach of applying coating liquid for which polyester film is manufactured is adopted suitably. Specifically, the approach of applying coating liquid to a non-extended sheet front face, and drying, the approach of applying coating liquid to an uniaxial stretched film front face, and drying, the approach of applying coating liquid to a biaxially oriented film front face, and drying, etc. are mentioned. In these, the approach of carrying out desiccation hardening of the spreading layer simultaneously in the process which heat-treats on a film is [after applying coating liquid to an unstretched film or an uniaxial stretched film front face] economical.

[0022] Moreover, the approach which used together some of above-mentioned methods of application can also be adopted as an approach of forming a spreading layer if needed. The first pass is applied to a non-extended sheet front face, it dries, and, specifically, the approach of applying the second layer and drying etc. is mentioned after extending to 1 shaft orientations after that. As an approach of applying coating liquid on the surface of polyester film, Yuji Harasaki work, Maki-Shoten Publishing, the 1979 issuance, the reverse roll coater shown in a "coating method", a gravure coating machine, a rod coating machine, an air doctor coating machine, etc. can be used.

[0023] As for the coating liquid used in this invention, it is usually desirable to adjust water as a main

medium from a viewpoint of safety or health nature. As long as water is used as a main medium, the little organic solvent may be contained in order to improve the object or the film formation engine performance of improving the distribution to water. An organic solvent needs to use it in the range dissolved in water, when using it, mixing with the water which is a main medium. Although an organic solvent may be used independently, two or more sorts may be used together if needed.

[0024] The mold releasing film which prepared layers, such as a hardening silicone resin paint film by silicone resin, as an example of an activity of the polyester film obtained by this invention is mentioned. A hardening silicone resin paint film is a layer which gives a mold release property to a film, and is made to form by coating the coating liquid containing hardenability silicone resin, and making it dry and harden. In this case, although both in-line coating and off-line coating can be used, it is desirable to form a hardening resin paint film by off-line coating. Although not limited especially as hardening mold silicone resin, anything can use a condensation reaction mold, an addition reaction mold, an ultraviolet curing mold, an electron ray hardening mold, etc., for example.

[0025] In this invention, it can coat as an approach of coating hardening mold silicone resin by well-known approaches, such as the reverse roll coat method, the gravure roll coat method, and the air-knife coat method. For example, the applied heat-curing mold silicone resin can form preferably 50 degrees C - 150 degrees C of hardening coats less than 2 minutes by heat-treating by the time amount for less than 1 minute at the temperature of the range of 80 degrees C - 130 degrees C. As coverage of hardening mold silicone resin, they are 1-25g/m³, further 2 - 20 g/m³. The range is desirable and the thickness of the silicone resin paint film after hardening has the desirable range of 0.05-1 micrometer and further 0.1-0.5 micrometers. When paint film thickness is less than 0.05 micrometers, there is an inclination for the mold release engine performance to fall. Moreover, when paint film thickness exceeds 1 micrometer, hardening [of a paint film] becomes inadequate and there is a possibility that the mold release engine performance may come to change with time.

[0026]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to the following examples, unless the summary is exceeded. In addition, various kinds of physical properties in this invention and the measuring method of a property, and the definition are as follows. Moreover, that it is with the "section" and "%" means ** "the weight section" and "% of the weight" among an example and the example of a comparison.

[0027] (1) Set the polyester film to heat-treat by the Kent paper of the heat treatment A4 size of a film. In that case, four corners are clipped on a wiry clip etc. so that a field with a spreading layer may become outside, and Kent paper and polyester film are stopped. It heat-treats by leaving said polyester film for 10 minutes in 150-degree C oven under nitrogen-gas-atmosphere mind.

[0028] (2) The amount upper part of film surface oligomer is opened, and the area of a base is 2 250cm. The polyester film after heat treatment is folded and the box of a rectangular head is created so that it may become. When the spreading layer is prepared, it is made for a spreading stratification plane to serve as the inside. Subsequently, DMF(dimethylformamide)10ml is put in into the box created by the above-mentioned approach, and the neglect back DMF is collected for 3 minutes. Collected DMF is supplied to liquid chromatography (Shimazu LC-7A), the amount of oligomer in DMF is calculated, this value is broken by film area in which DMF was contacted, and it considers as the amount of film surface oligomer (mg/m²).

[0029] (3) According to film haze JIS-K7105, the turbidity of the film after heat treatment was measured by Nippon Denshoku Industries integrating-sphere type turbidity meter NDH-20D.

(4) The sample was rubbed after neglect for 30 days after love off test coating, the coating side was rubbed several times by the fingertip to the interior of a room of RH 23 degrees C / 50%, the condition of omission of a hardening silicone coat was judged in the following valuation basis, and it considered as the rule of thumb of adhesion.

O : with no omission (adhesion is good)

**: Although it drops out a little, they are those with level x:omission which are satisfactory practically (poor adhesion).

[0030] In an example and the example of a comparison, the binder resin used for the oligomer deposit prevention stratification is as follows.

(Example of a compound)

** PVA system resin: -- polyvinyl alcohol ** drainage system polyester:[of A saponification degree =88 mol % and degree-of-polymerization =500] B -- a silica sol [0031] with a drainage system polyester ** cross-linking compound:C hexamethoxy methyl melamine ** inactive particle:D mean particle diameter of 65nm which neutralized and drainage-system-ized the polyester which made the polyester which is mainly concerned with isophthalic acid, ethylene glycol, and a diethylene glycol carry out copolymerization of the dicarboxylic acid derivative which has neopentyl glycol and an aliphatic series dicarboxylic acid anhydride, and obtained it with the amine compound The coating liquid which contains example 1(adjustment of coating liquid -1) PVA system resin (A) 80% of the weight, and contains a cross-linking compound (C) for drainage system polyester (B) 10% of the weight 10% of the weight was adjusted. Solid content concentration of coating liquid was made into 2 % of the weight.

[0032] (Manufacture of a film) After performing an ester exchange reaction according to a conventional method, the silica particle with a mean particle diameter of 1.5 micrometers which ethylene glycol was made to distribute was added. Subsequently, the polycondensation reaction was advanced according to the conventional method, and the polyethylene terephthalate of intrinsic viscosity 0.65 was obtained. Melting extrusion of this polyethylene terephthalate was carried out at the temperature of 280-300 degrees C, the cast was carried out to cooling drum lifting, using electrostatic contact printing together, and the non-fixed form film with a thickness of about 550 micrometers was obtained. After extending this film 3.7 times to the lengthwise direction at 85 degrees C and applying coating liquid -1 to one side of a film, it extended 3.9 times in the longitudinal direction at 100 degrees C, it heat-treated at 210 degrees C, and biaxial-stretching polyester film with a thickness of 38 micrometers was obtained.

[0033] (Manufacture of a mold releasing film) Using the coating liquid which is from the hardenability silicone resin (KS[by Shin-Etsu Chemical Co., Ltd.]- 779) 100 weight section, the curing agent (CAT [by Shin-Etsu Chemical Co., Ltd.] PL- 8) 1 weight section, and a methyl ethyl ketone / toluene / n-heptane mixed solvent 2200 weight section on the oligomer closure layer side of the obtained film, it applied so that the spreading thickness after hardening might be set to 0.1 micrometers in my YABA, and the mold releasing film in which the hardening silicone resin coat was formed was obtained.

[0034] In examples 2-4 and one to example of comparison 4 example 1, the film was obtained like the example 1 except having changed the presentation of coating liquid, as shown in the following table 1.

[0035]

[A table 1]

Table 1----- PVA Drainage system resin Bridged compound Particle Surface oligomer (A) (B) (C) (D) (mg/m²)

The example 1 70 15 10 5 0.28 Example 2 80 0 20 0 0.12 Example 3 100 0 0 0 0.12 Example 4 20 70 10 0 0.48 Example 1 of a comparison Have no spreading. 1.96 Example 2 of a comparison 8020 0 19.12 The example 3 of a comparison 60 30 10 00.80 Example 4 of a comparison 585 100 The assessment result of the film obtained in the 1.44 ----- example and the example of a comparison is collectively shown in the following table 2.

[0036]

[A table 2]

Table 2----- Spreading thickness Haze Love off test (micrometer) (%)

example 1 0.05 3.2 O Example 2 0.05 3.1 ** example 3 0.05 4.2 ** example 4 0.05 4.8 The example 1 of a ** comparison - 5.6 x Example 2 of a comparison 0.05 6.1 x Example 3 of a comparison 0.05 6.2 x Example 4 of a comparison 0.05 6.3 x----- [0037]

[Effect of the Invention] According to the film of this invention, the oligomer which deposits on a film front face also under an elevated temperature can be stopped, the mold releasing film which coated silicone resin can be provided with a useful film, and the industrial value is high.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] It sets on the film which comes to prepare a spreading layer in one [at least] front face of polyester film, and the amount of oligomer of the spreading layer front face after heat treatment is 0.60 mg/m² for 10 minutes at 150 degrees C. Polyester film which is the following and is characterized by a spreading layer containing polyvinyl alcohol ten to 100% of the weight.

[Claim 2] The mold releasing film characterized by having a hardening silicone resin coat on the spreading layer of polyester film according to claim 1.

[Translation done.]